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(54) Title: NEO-ACID ESTER ACRYLIC ADHESIVES

(57) Abstract

Acrylic copolymers and adhesive compositions having both enhanced peel strength and shear properties are formulated by incorporating a neoalkanoate vinyl ester monomer, such as vinyl neopentanoate, into an acrylic copolymer of alkyl (meth)acrylate and (meth)acrylic acid monomers.

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NEO-ACID ESTER ACRYLIC ADHESIVES

Field of the Invention

This invention relates to acrylic copolymers, and more particularly to adhesive compositions based on acrylic copolymers having vinyl neoalkanoate as a comonomer. The invention addresses the problem in the prior art of simultaneously achieving high peel strength adhesion and high shear strength cohesion.

Background of the Invention

According to the "Glossary of Terms Used in the Pressure Sensitive Tape Industry," a pressure sensitive adhesive (PSA) is a material which is aggressively and permanently tacky, adheres without the need of more than finger pressure, exerts a strong holding force, and has sufficient cohesiveness and elasticity that it can be removed from substrates without leaving a residue.

Acrylic copolymers commonly used as adhesives, particularly PSAs, generally have a relatively low glass transition temperature (T_g). Such copolymers are usually prepared by a free radical emulsion polymerization of several acrylic monomer mixtures.

For many PSA applications, a good balance of peel and shear properties on substrates such as polyester or stainless steel is a greatly desired attribute. Unfortunately, this goal has typically been difficult to obtain because advances made to improve tackiness have generally reduced cohesive strength and vice versa.

Theoretically, the adhesive/cohesive property balance of a copolymer can be explained in terms of the ratio of molecular weight to entanglement molecular weight (M/M_e) and T_g. It has been found that peel strength generally increases with decreasing M/M_e and T_g. Shear strength, however, generally <u>decreases</u> with decreasing M/M_e and T_g. For acrylic based PSAs which

contain a major proportion of an alkyl acrylate comonomer, both M/M_e and T_g terms trend in the same direction -- decreasing as alkyl chain length of the comonomer increases and vice versa. Table 1 below gives M_e and T_g data obtained from rheometry and differential scanning calorimetry measurements for a series of alkyl acrylate homopolymers with increasing alkyl chain length:

Table 1

POLYMER	Me	Tg (C)
Poly(methyl acrylate)	14,000	14
Poly(ethyl acrylate)	15,000	-23
Poly(n-butyl acrylate)	17,000	-52
Poly(2-ethylhexyl acrylate)	32,000	-72

Most commercially available PSAs combine several different acrylic monomers to obtain the level of peel/shear balance desired for a specific application, but cannot change the inherent opposition of peel/shear properties due to the above-illustrated relationship of M_e and T_g, i.e., increasing the size of the alkyl ester substituent increases M_e (and peel strength) but decreases T_g (and shear strength). Thus, it has been difficult to simultaneously improve both peel adhesion and shear cohesion properties.

US patent 4,507,429 discloses a method to improve the shear strength without substantially affecting peel and tack. The polymer used comprises vinyl acetate, acrylic acid, dioctyl maleate, and triallyl cyanurate. A soft copolymer is made in the core and a cross linked hard copolymer is made in the shell. The shear thinning is improved through the crosslinking reaction between the acrylic acid and the triallyl cyanurate.

US patent 4,629,663 concerns a water borne PSA tape composition which contains isoctyl acrylate, N-tert-octyl acrylamide and a monomeric surfactant, sodium

styrene sulfonate in a copolymer. The cohesive strength is reported improved by the incorporation of sodium styrene sulfonate.

US patent 4,645,711 extends the composition of US 4,629,663 to include the blending of polymer latex with resin emulsions either subsequent to or prior to the copolymerization. By incorporating the tackifier resin, the tape is reported to have better resistance aganist liftring forces at elevated temperatures while also being cleanly removable.

US patent4,113,792 discloses the addition of a chlorosulfonated polyethylene and polymerizable vinyl monomer or unsaturated oligomer to conventional acrylic PSA. Upon curing, improvement in cohesive strength as well as heat and solvent resistance without significant loss in peel and tack prior to curing is reported.

Japanese Patent J-51125472 describes a petroleum resin emulsion that is obtained by polymerizing vinyl monomers in the presence of petroleum resins having softening points of from 40 to 160°C, an average molecular weight of 300 to 3000, and an acid value and saponification value of less than 1. The monomers include, for example, alkyl (meth)acrylates, vinyl acetates, vinyl chlorides, styrene, acrylonitrile, and acrylic acid.

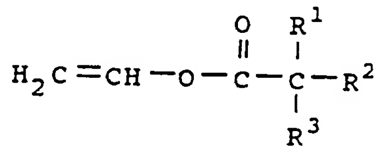
Accordingly, there still remains a need for improvements to acrylic copolymers and the procedures used to prepare such copolymers in the form of a latex-like dispersion for adhesive application wherein peel strength is increased without deterioration in shear strength, or even, with improved shear.

Summary of the Invention

It has been discovered that incorporation of a vinyl neoalkanoate comonomer into an acrylic copolymer

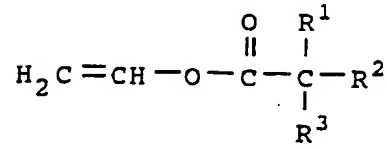
simultaneously enhances both tack and shear properties in adhesive applications.

In one embodiment, the present invention provides an acrylic copolymer containing a neoalkanoate vinyl ester. The copolymer is generally prepared from a monomer mixture including from 1 to 60, preferably from 5 to 35 percent by weight, of a neoalkanoate vinyl ester represented by the formula:



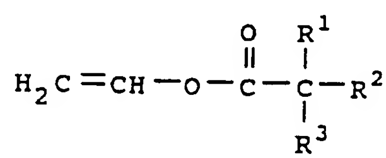
wherein R^1, R^2 and R^3 are independently hydrocarbyl groups each having from 1 to 10 carbon atoms and $R^1 + R^2 + R^3$ = from 3 to 23 carbon atoms; from 25 to 98, preferably from 59 to 93 percent by weight, of alkyl (meth)acrylate; and from 1 to 15, preferably from 2 to 6 percent by weight, of (meth)acrylic acid. The acrylic copolymer can also include one or more of acrylonitrile, vinyl acetate, vinylidene chloride, styrene and methyl styrene. The copolymer has a T_g of from -70°C to +70°C, preferably from -60°C to +10°C. The alkyl (meth)acrylate can include a mixture of lower alkyl and upper alkyl esters, wherein the total content of the upper alkyl ester and the vinyl neoalkanoate is preferably from 26 to 99 percent by weight.

In another embodiment, the invention provides an adhesive latex emulsion. The emulsion comprises up to 70 percent by weight, preferably from 30 to 70 percent by weight, of an acrylic copolymer made up of from 0.1 to 60 percent by weight of a neoalkanoate vinyl ester represented by the formula:



wherein R^1, R^2 and R^3 are independently hydrocarbyl groups each having from 1 to 10 carbon atoms and $R^1 + R^2 + R^3$ = from 3 to 23 carbon atoms; from 25 to 98 percent by weight of alkyl (meth)acrylate; and from 1 to 15 percent by weight of (meth)acrylic acid. The acrylic copolymer has a T_g of from -70°C to +70°C, preferably from -60°C to +10°C, and is preferably prepared by emulsion polymerization of the monomers.

The polymer latex can be coated onto a suitable substrate and dried into a coating useful as a pressure sensitive adhesive (PSA) having enhanced peel strength while maintaining or increasing shear properties, including high temperature shear properties. Thus, in a further embodiment, the present invention comprises a pressure sensitive adhesive-coated article comprising a substrate having a coating of an acrylic copolymer on a surface thereof. In a preferred embodiment, the acrylic copolymer in the coating comprises from 1 to 60 percent by weight of a neoalkanoate vinyl ester represented by the formula the formula:



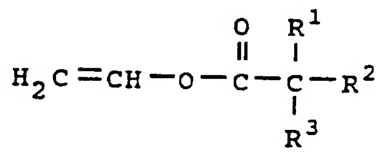
wherein R^1, R^2 and R^3 are independently hydrocarbyl groups each having from 1 to 10 carbon atoms and $R^1 + R^2 + R^3$ = from 3 to 23 carbon atoms; from 25 to 98 percent by weight of alkyl (meth)acrylate ester; and from 1 to 15 percent by weight of a (meth)acrylic acid. The copolymer coating may have a T_g

from -70°C to +200°C, preferably from -70°C to +70°C, even more preferably -10°C to +60°C. The PSA coating of the present invention is ideally suited for PSA tape applications. Tape substrates can be metallic, paper, plastic or cloth.

In yet a further embodiment, the present invention is a laminate article comprising at least two layers of material bonded by the aforedescribed adhesive.

Detailed Description of the Invention

A first type of polymerizable monomer in the present copolymer is a neoalkanoate vinyl ester, preferably a neoalkanoate vinyl ester represented by the formula:



wherein R^1, R^2 and R^3 are independently hydrocarbyl groups each having from 1 to 10 carbon atoms and $R^1 + R^2 + R^3$ = from 3 to 23 carbon atoms. The total carbon atoms in R^1, R^2 and R^3 is from 3 (R^1, R^2, and R^3 are each methyl) to 23, i.e., the acid moiety has from 5 to 25 carbon atoms. Examples of suitable neoalkanoate vinyl ester monomers include vinyl neopentanoate, vinyl neohexanoate, vinyl neoheptanoate, vinyl neooctonoate, vinyl neononanoate, vinyl neodecanoate, vinyl neotridecanoate, isomers and combinations thereof, and the like. It is understood that such monomers have various isomeric forms and are typically available commercially, for example, as an isomer mixture. Neoalkanoate vinyl esters are available commercially from Royal Dutch Shell Company under the trade designation VEOVA. Especially preferred neoalkanoate vinyl esters are vinyl neopentanoate sold under the trade designation VEOVA 5, vinyl neononanoate

sold under the trade designation VEOVA 9, and vinyl neodecanoate (VND) sold under the trade designation VEOVA 10.

Such neo-acid vinyl ester compounds have been found to have a complementary M_e and T_g relationship. VND, for example, has an M_e greater than 40,000 while its T_g is -11°C. Similar vinyl neo-acid esters tested have been found to have higher T_g than alkyl acrylates at comparable M_e's.

The second type of polymerizable monomer in the present copolymer is generally described as an acrylic, e.g., alkyl (meth)acrylates and (meth)acrylic acid. The present copolymers typically include a mixture of several different acrylic monomers including at least one (meth)acrylic acid monomer and one or more alkyl (meth)acrylate ester monomers.

As used herein, the terms "acrylics" or "acrylic polymer" or "acrylic monomer" denote a generalized material comprising in greatest proportion an alpha,beta-ethylenically unsaturated carboxylic acid, dicarboxylic acid or anhydride; a hydrocarbyl ester of an alpha,beta-ethylenically unsaturated carboxylic acid or dicarboxylic acid; or a mixture thereof. The term "(meth)acrylate" refers to either a methacrylate or an acrylate ester, but it is understood that other types of acrylic ester monomers can be used. The term "(meth)acrylic acid" refers to either methacrylic acid (MAA) or acrylic acid (AA), but it is understood that other acrylic monomers containing an alpha,beta-ethylenically unsaturated carboxylic acid group can be used. Lower alkyl (meth)acrylates are defined herein as having 1 to 3 carbon atoms in the alkyl ester group, and upper alkyl (meth)acrylates as having from 4 up to 14 or more carbon atoms in the alkyl ester group, but preferably from 4 to 8 carbon atoms.

Examples of suitable alkyl (meth)acrylate ester monomers include methyl (meth)acrylate, ethyl

(meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate (NBA), 2-ethylhexyl (meth)acrylate, and the like. Preferred alkyl (meth)acrylate monomers include n-butyl (meth)acrylate and 2-ethylhexyl (meth)acrylate.

Examples of suitable alpha,beta-ethylenically unsaturated carboxylic acid monomers include acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, and the like. (Meth)acrylic acid is preferred.

A minor proportion of other free radical polymerizable monomers can be employed in the present copolymer, including acrylonitrile, vinyl acetate, vinylidene chloride, styrene, methyl styrene, and the like.

The copolymer comprises from 1 to 50 percent by weight, preferably from 5 to 35 percent by weight and more preferably from 10 to 25 percent by weight of the neoalkanoate vinyl ester; from 25 to 98 percent by weight, preferably from 59 to 93 percent by weight of the alkyl (meth)acrylate ester(s); and from 1 to 15 percent by weight, preferably from 2 to 6 percent by weight of (meth)acrylic acid.

The alkyl (meth)acrylate ester component can be made up of a mixture of the upper alkyl and lower alkyl esters. The copolymer can contain from 0 to 50 percent by weight, preferably from 10 to 35 percent by weight of a lower alkyl (meth)acrylate ester; and from 0 to 98 percent by weight, preferably from 30 to 85 percent by weight of an upper alkyl (meth)acrylate ester. The total copolymer content of upper alkyl (meth)acrylate and vinyl neoalkanoate combined preferably comprises from 26 to 99 percent by weight of the copolymer, more preferably from 50 to 88 percent by weight.

The copolymer can contain a minor proportion, e.g.,

up to 5 percent by weight of components such as acrylonitrile, vinyl acetate, and the like. It should be noted that some acrylic monomer mixtures commercially available also include minor amounts of acrylonitrile, styrene, vinyl acetate, and the like.

The composition of the present copolymer in terms of monomer selection and concentration is guided by a determination of the desired glass transition temperature (T_g) since this is in part determinative of adhesive properties such as tack and shear. Suitable T_g for the present copolymer product will range from -70°C to 70°C for PSA applications, preferably from -60°C to 10°C. If the glass transition temperature is too high, ambient temperature tackiness required for standard PSA applications is not generally obtained. The glass transition temperature of the product is usually a function of the glass transition temperature of the component monomer homopolymers. Thus, to achieve the low T_g, it is generally necessary to avoid excessive amounts of high T_g monomers such as (meth)acrylic acid and C_1-C_3 alkyl (meth)acrylates, as well as the high T_g materials such as styrene, acrylonitrile and the like.

The acrylic copolymers will normally have a ratio of M_w/M_n between 2 and 4, but in one embodiment, the acrylic copolymers can optionally have a relatively broad molecular weight distribution, i.e., a higher ratio of the weight average molecular weight to number average molecular weight (M_w/M_n). Copolymers which have a high M_w/M_n ratio generally have enhanced tack and shear properties. This molecular weight distribution effect has been seen when the ratio of M_w/M_n is 6 or more, but more preferably over the range of from 6 to 10. The upper limit on the ratio is set primarily by polymerization practicalities since it is desirable to produce high molecular weight species which are essentially free of gel. The lower limit of M_n corresponds to a sufficient degree of polymerization for

internal strength, and M_n is preferably at least 10,000. Thus, there is no particular upper limit on the M_w/M_n that can be obtained.

To prepare the PSAs of the present invention, the present copolymers are preferably blended with a suitable tackifier component. The PSA can optionally include up to 100 parts of a tackifier per 100 parts by weight of the copolymer, and preferably from 20 to 80 parts tackifier per 100 parts by weight of the copolymer. The tackifier is preferably added to an emulsion before polymerization of the monomers. Useful tackifier resins are generally well known and include natural resins and thermoplastic petroleum hydrocarbon resins obtained by polymerization of steam-cracked petroleum distillates boiling in the range between 30°C and 280°C, or any fraction thereof, or of polymerizable mixtures of olefins and diolefin in the presence of a catalyst of the Friedel-Crafts type. However, suitable adhesive properties can be achieved by the present copolymer without the tackifier. Therefore, tackifier use is optional and the neat copolymer can be used to avoid the difficulties and complexities normally associated with tackifiers.

Certain tackifiers can be homogeneously incorporated into the present copolymer matrix to enhance the overall properties of the PSA. The tackifier can be blended with the monomers and/or copolymers before or after polymerization. The tackifier is optionally dissolved in the monomer mixture prior to polymerization for internal tackification without substantially interfering with the polymerization process. Suitable internal tackifiers should have at least 10 percent by weight aromaticity, and preferably from 30 to 100 percent by weight aromaticity, to enhance dissolution in the monomer mixture. In addition, suitable tackifiers should be hydrogenated resins with a low degree of unsaturation to avoid interference with the free radical

polymerization.

The hydrocarbon resins useful for tackification are preferably petroleum resins prepared by homo and copolymerization of olefins, diolefins, and vinyl aromatic components, predominantly the C_5 to C_9 species, from distillates of cracked petroleum stocks. The feedstocks for the resin preferably have at least about 10 percent by weight vinyl aromatic constituents, such as, for example, styrenes, alpha-methyl styrene, indene and vinyl toluene and other well known vinyl aromatic compounds, particularly when internal tackification is desired. A Friedel-Crafts catalyst is typically employed and this resin-forming polymerization is performed at temperatures which range generally from 0°C to 70°C and preferably from 30°C to 55°C. The resulting resin is then hydrogenated in accordance with the methods described in U. S. Patents 4,650,829; 4,328,090 and 4,629,766, for example.

The resulting hydrogenated resin retains a ring and ball softening point in the range of -20°C to 150°C, preferably from 10°C to 100°C. PSAs formed from resins having a softening point from 15°C to 40°C typically find their best use as adhesives for laminant articles or adhesives for labels. PSAs utilizing resins having softening points from 70°C to 100°C are typically used for tapes.

Suitable petroleum tackifier resins are commercially available under the trade designations of, for example, ESCOREZ®, ARCON® and the like.

Suitable naturally occurring resins for internal tackification are rosin esters or terpenes such as alpha-pinene, beta-pinene, carene, limonene or other readily available terpinous materials, alpha-pinene and limonene being preferred. The material may be pure or the commercially available concentrates such as gum terpentine or alpha-pinene concentrates, which tend to be

mixtures of various terpinous materials. A suitable natural resin contains from about 70 to 95 percent by weight alpha-pinene, the remainder being other terpenes. Limonene and carene streams are available and are known to those in the art. These are typical streams useful in the present invention. The hydrogenation of these naturally occurring resins is well known and can be carried out using the procedures of the above-identified U. S. Patents.

Generally the reaction of the selected acrylic monomers to form acrylic copolymers proceeds by aqueous emulsion polymerization which is a type of polymerization well known to the practitioners in the art. The reaction mixture generally includes an initiator which may be any compound(s) or source for generating free radicals capable of initiating polymerization of the acrylic monomers, such as, for example, azo compounds, persulfates, redox couples and the like.

When making a copolymer having a broad molecular weight distribution, the redox couples preferably have a polymerization initiation temperature below 60°C, i.e. between -40°C and 60°C, especially between -30°C and 30°C, particularly redox couples including an oxidant such as bromate or chlorate ion from any suitable source, e.g. sodium, potassium or ammonium bromate or chlorate, and a reductant such as bisulfite ion from any suitable source, e.g. sodium or potassium bisulfite or metabisulfite. The redox couple potassium bromate/sodium metabisulfite is particularly preferred because it is capable of generating free radicals to initiate polymerization at low temperatures, e.g. 0° to 10°C. When used, the redox couple in approximately stoichiometric proportions is generally present at from 0.01 to 1 part per 100 parts by weight of monomer in the reaction mixture.

The process generally includes water to adjust the solids content of the emulsion. In some instances it may

be advantageous to buffer the pH of the solution between 4 and 7 by including some well known buffering agent such as, for example, sodium bicarbonate, potassium hydrogen phthalate and the like.

A surfactant is normally used to aid in the formation of monomer-in-water emulsion and to act as a suspending agent for the solids in the final copolymer, which are dispersed in the aqueous medium both during and after the polymerization, but this should not be considered a limitation on the invention. The surfactants useful in the practice of this invention are well known and are present in quantities sufficient to place the reactants in the emulsion prior to reaction and maintain the product in suspension after the reaction. Of particular applicability are a blend of anionic and nonionic surfactants having a hydrophile-lipophile balance (HLB) of from 14 to 42, especially from 35 to 40. Especially preferred is the widely used disodium sulfosuccinate as an ionic surfactant and ethylene oxide adducts of nonyl phenol as nonionic surfactants. While the ranges of surfactants are well known, the amount will preferably range from 1 to 5 parts, normally 2 to 4 parts per 100 parts of the monomers, by weight.

The molecular weight of such copolymers is normally controlled by a commonly known mono-olefin chain transfer agent in the polymerization mixture. It is preferred that the monomers be dispersed into a water medium to form an emulsion at ambient temperatures just by stirring in the presence of a satisfactory surfactant. The reaction mixture thus formed, including the initiators, must be placed in a reaction vessel, evacuated of oxygen by purging with nitrogen or other inert gas, and the polymerization reaction conducted with stirring in the sealed container under a nitrogen or other inert gas blanket.

The addition of the monomers can be batchwise, or

alternatively carried out intermittently and over a period of time. For example, 5 to 25, preferably 10 to 20 percent, by weight of the monomer solution, can be initially batched into the reaction mixture and polymerized for a short period of time at a relatively low temperature, preferably from 0°C to 30°C, e.g., ambient temperature to make a "pre-emulsion." Normally when this is accomplished, the solids content of the reaction should preferably be 20 to 22 percent by weight, which is a benchmark solids content. Once the selected solids level is attained, the balance of the monomer solution is evenly metered into the reaction vessel over a period of time, usually 3 to 6 hours, depending upon the size of the reactor and quantity to be added, while maintaining the desired reaction temperature, which can be held relatively constant or alternately increased gradually and/or stepwise. The polymerization is allowed to continue, while maintaining the reaction temperature within the range of from 45°C to 90°C, preferably between 50°C and 80°C, until the total solids content of the material in the reactor reaches its theoretical level based upon the amount of reactants charged to the reaction mixture. Usual practice is 45 to 55 percent by weight solids, but the overall solids content may be as high as 70 percent by weight. While there is no theoretical lower limit, a practical lower limit of 40 percent by weight solids content is recognized by those skilled in the art. In a commercial sense, the highest limits attainable are preferred.

The reaction temperature is not particularly critical, but when the optional temperature-ramping is used, the difference between the minimum and maximum polymerization temperature is preferably at least 40°C to obtain the desired molecular weight distribution. The limits on the polymerization temperature are determined largely by practical

considerations. For example, the minimum polymerization temperature must be equal to or above the freezing point of the polymerization medium and the activation temperature of the catalyst; the maximum polymerization temperature must likewise be below the boiling point of the reaction medium (which may be pressurized) and the copolymer degradation temperature.

Once the reaction is complete, the solids, in the form of a dispersed polymer latex, is allowed to cool to room temperature and the dispersed polymer latex is usually separated from coagulum formed during polymerization by filtration. In the practice of this invention, a 200 mesh "sock" filter has been found satisfactory.

The latex product can be coated on a substrate film for use as a tape, for example. The coated substrate is typically dried by circulating hot air at 100°C to 110°C for 2 to 5 minutes. Those skilled in the art readily recognize other processing parameters for such coated substrate. The dried and cured latex coating of the present acrylic copolymer emulsions produces an adhesive film suitable for PSA application. Suitable substrates include metallic, plastic, paper, cloth, wood, pressed wood, glass, film, woven fabric, nonwoven fabric, polyolefin, materials and the like. Examples of metallic substrates include aluminum, copper and steel and examples of the plastic substrates include polyesters, polyolefins, polyethylene terephthlate, and the like.

In certain embodiments of the practice of this invention, the adhesives formed find application as non-pressure sensitive adhesives such as, for example, laminating adhesives, binders for woven and nonwoven fabrics and binders for pressed wood production. For example, embodiments useful as laminating adhesives have high peel strength but low shear properties. Such adhesives can be used to join two or more sheets of material together such as joining a layer of wood or a multiple layer of wood to form a plywood product.

The foregoing invention having now been described, the following examples are to further teach the preferred embodiment and best modes for practicing the described invention and to aid others in the practice of the scope of such invention herein provided.

Example 1

This example illustrates the synthesis of a butyl acrylate copolymer emulsion incorporating vinyl pentanoate comonomer. The ingredients in the order that they are charged into the reactor are summarized in Table 2 below.

TABLE 2

Step	Ingredients	Amount (g)
A	Initial water	61.6546
B	TWE-2448 (acrylic latex heel)	11.7408
C	Pre emulsion mixture	23.3578
D	Water	6.4207
	Sodium Persulfate	0.1584
E	(water phase)	
	Water	64.6380
	GEROPON LIV/30 (surfactant)	6.5945
	(monomer phase)	
	VEOVA-7 (vinyl neoheptanoate)	49.62
	Butyl acrylate	266.76
	Acrylonitrile	6.6475
	Acrylic acid	6.5945
	t-dodecanethiol (chain transfer agent)	0.1154
F	Water	13.5234
	NaOH (30 wt. %)	1.8678
	Sodium persulfate	2.4561
G	(post treatment)	
	Water	0.6172/ 0.6306
	t-BHP	0.1938/ 0.1891
H	Water	1.8596/ 1.8054
	FORMOSUL (fungicide)	0.2727/ 0.2802
I	PROXEL AB (fungicide)	0.2479

A 2-liter, four-neck reaction flask equipped with a stirrer, condenser, a thermosensor, and a monomer addition tube was purged with nitrogen for 15 minutes. The initial water charge (charge A) was added to the flask with stirring at room temperature and the reactor was heated to 70°C.

In separate flasks, the pre-emulsion mixture (charge C) was made by preparing the water and monomer phase mixtures (charge E) and adding the water and monomer phase mixtures together slowly under agitation.

A commercially available acrylic latex heel is added to the reactor (charge B) and mixed about 5 minutes until

homogeneous. The heel is used to control the final product distribution. Then the initial monomer charge (pre-emulsion mixture, charge C) is added to the reactor and mixed for 30 minutes while maintaining the reactor temperature at 70°C.

The initial catalyst charge (charge D) was added to the reactor and the temperature was raised to 80°C. After 30 minutes a sample was taken and the percent solids of the reaction effluent were measured. The feed streams were then slowly, uniformly metered into the reactor flask over 4 hours while the reactor temperature was maintained at 80°C. Four additional samples were taken after each hour and at the end of the feed addition to track the total solids in the reactor. At the end of the feed addition, the reactor was maintained at 80°C for an hour and a last sample was taken. The reactor was then cooled to 60°C and post-polymerization treatment was started. The first portion of charge G was slowly added to the reactor over 5 minutes, and 2 minutes later the first portion of charge H was slowly added to the reactor over 5 minutes. After 20 minutes at 60°C a last sample was taken. Second portions of charges G and H were added. The batch was cooled, PROXEL AB fungicide (charge I) was added and the effluent was cooled through a screen.

The final total solids was about 68.61 percent by weight and 422.71 g of copolymer latex product were collected.

Examples 2-7 and Comparative Examples 1-3

Additional polymer latexes were similarly prepared as outlined in Example 1 except that the types of monomers used were varied. In Examples 2-7, varying amounts of vinyl neodecanoate were substituted for the vinyl pentanoate. In Comparative Examples 1-3, 2-ethylhexyl acrylate was substituted for the vinyl

neodecanoate. The composition of the copolymers prepared is summarized in Table 3.

TABLE 3

Example	Monomer Composition				
	n-Butyl acrylate	Vinyl neo-decanoate	2-Ethyl-hexylacrylate	Acrylonitrile	Acrylic Acid
2	91	5	0	2	2
3	86	10	0	2	2
4	76	20	0	2	2
5	96	3	0	0	3
6	92	5	0	0	3
7	87	10	0	0	3
Comp. 1	91	0	5	2	2
Comp. 2	86	0	10	2	2
Comp. 3	76	0	20	2	2

<u>Examples 8-10 and Comparative Examples 4-6</u>

PSA samples were prepared using the copolymer latexes from Examples 2-7 and Comparative Examples 1-3 and PSA properties were measured. The polymer latexes were knife-coated on a Mylar film and dried in an air circulating oven for three minutes at 110°C. The dried adhesive coating was approximately 1.5 mils thick. The adhesive was bonded to stainless steel and/or polyethylene surfaces for PSA performance tests. Peel (180°) adhesion was obtained using Test No. PSTC-1 of the Pressure Sensitive Tape Council. Loop tack was obtained according to PSTC-6. Shear was determined according to PSTC-7. The shear was tested at either 1 square inch or 1/2 square inch and a 1 kg hang weight.

PSA performance improved for both adhesion and cohesion strength properties for increasing concentrations of the vinyl neodecanoate monomer. In the comparative example copolymer samples, shear generally decreased with increasing 2-ethylhexyl acrylate. In absolute terms, the samples made using vinyl neodecanoate had much better shear properties and equivalent or better tack properties compared to the copolymer samples containing 2-ethylhexanoate. Table 4 summarizes the PSA

test results.

TABLE 4

Example No.	Copolymer	Comonomer (wt %) vinyl-neodecanoate	Comonomer (wt %) 2-ethyl-hexyl-acrylate	PSA Property 180° Peel/SS (lb/in.)	PSA Property Loop Tack/SS (lb/in.)	PSA Property Shear/SS 1"x0.5"x1 kg (hrs)
8	Ex. 2	5	0	1.7	2.8	16
9	Ex. 3	10	0	1.8	3.0	18
10	Ex. 4	20	0	2.1	3.2	21
Comp. 4	Comp. Ex.1	0	5	2.1	2.8	3.9
Comp. 5	Comp. Ex.2	0	10	2.1	2.8	3.9
Comp. 6	Comp. Ex.3	0	20	1.7	2.7	1.6

__Examples 11-16__

PSA samples were prepared similarly to Examples 8-10 and Comparative Examples 4-6 to determine PSA properties of tackified vinyl neodecanoate copolymers from Examples 2-7 and Comparative Examples 1-3. The copolymers were mixed with SNOWTACK 301CF tackifier at a weight ratio of 60 parts copolymer to 40 parts tackifier. Results are given in Table 5.

TABLE 5

Ex.	Co-polymer	Comonomer (wt %)				PSA Property					
		NBA	VND	Acrylo-nitrile	AA	180° Peel (lb/in.)		Loop Tack (lb/in.)		Shear/SS (hrs)	
						SS	PE	SS	PE	A	B
11	Ex. 2	91	5	2	2	3.9	1.6	4.5	2.2	38	-
12	Ex. 3	86	10	2	2	3.9	1.7	4.7	2.5	43	-
13	Ex. 4	76	20	2	2	4.7[a]	1.7[b]	4.7[b]	-	59	- -
14	Ex. 5	96	3	0	3	1.9	0.78	2.7	1.3	-	1.3
15	Ex. 6	92	5	0	3	2.1	1.1	3.2	1.5	-	2.0
16	Ex. 7	87	10	0	3	2.2	1.1	3.4	1.6	-	4.3

A-1"x 1"x 1 kg
B-1"x 0.5"x 1 kg
[a]-Adhesion transfer
[b]-Jerking

The results in Table 5 show that both adhesion (peel and loop tack) and cohesion (shear) properties can be simultaneously improved with the incorporation of VND comonomer.

Examples 17-21

Tackified PSA samples were prepared similarly to Examples 11-16 to compare PSA properties of n-butyl acrylate copolymers (81 wt %) having 15 wt % of a vinyl neo-acid ester comonomer of C_5 to C_{10} neo-acids. The copolymers also included 2 wt % acrylic acid and 2 wt % acrylonitrile. The PSA samples were blended with SNOWTACK 301CF at a weight ratio of 60/40 tackifier/polymer. Results are given in Table 6.

TABLE 6

Example	Vinyl Neo-acid Co-monomer[1]	PSA Properties				
		180°Peel (lb/in.)		Loop Tack (lb/in.)		Shear/SS 1"x1"x1 kg
		SS	PE	SS	PE	(hrs)
17	C_5	5.3	1.7	5.9	2.1	89
18	C_7	5.1	1.7	5.1	2.3[b]	46
19	C_8	4.8	1.7	6.1	2.3[b]	34
20	C_9	8.1[a]	2.0	6.9	2.5[b]	13
21	C_{10} (VND)	6.4[a]	1.9	6.5	2.4[b]	15

[1]-Number of carbon atoms in the neo-acid.
[a]-Adhesion transfer
[b]-Jerking

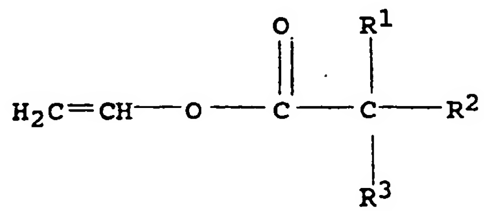
These copolymers all exhibited excellent PSA properties. Copolymers with C_5 and C_7 vinyl neo-acid esters showed strong shear properties for PSA tape applications and copolymers with C_8-C_{10} neo-acids showed good adhesion properties for PSA label applications.

As is apparent from the foregoing description, the materials prepared and the procedures followed relate to specific embodiments of the broad invention. It is apparent from the foregoing general description and the specific embodiments that, while certain forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of this invention. Accordingly, it is not intended that the invention be limited thereby.

Claims:

1. An acrylic copolymer composition comprising:

from 0.1 to 60 percent by weight of a vinyl neoalkanoate ester represented by the formula:



wherein R^1, R^2 and R^3 are independently hydrocarbyl groups each having from 1 to 10 carbon atoms and $R^1 + R^2 + R^3$ = from 3 to 23 carbon atoms;

from 25 to 98 percent by weight of an alkyl (meth)acrylate ester;

from 1 to 15 percent by weight of acrylic or methacrylic acid.

2. An adhesive latex emulsion composition comprising an aqueous dispersion of the composition of claim 1, 2, 3, 4, 5, or 6.

3. The composition of claim 1 or 2, including one or more of acrylonitrile, vinyl acetate, vinylidene chloride, styrene and methylstyrene.

4. The composition of claim 1, 2, or 3, characterized by a Tg from -70°C to +70°C .

5. The composition of claim 1, 2, 3, or 4, wherein the vinyl neoalkanoate ester is vinyl neopentanoate, vinyl neohexanoate, vinyl neoheptanoate, vinyl neooctanoate, vinyl neononanoate, vinyl neodecanoate, or a combination thereof.

6. The composition of claim 1, 2, 3, 4 or 5 wherein the alkyl (meth)acrylate includes a mixture of lower alkyl and upper alkyl esters, and wherein the total content of the upper alkyl ester and the vinyl neoalkanoate is from 26 to 99 percent by weight.

7. A coating comprising the composition of claim 1, 2, 3, 4, 5 or 6 being characterized by a Tg between -40°C to 200°C.

8. A substrate coated with the coating of claim 7, preferably the substrate is a film, wood, pressed wood, metal, glass, woven fabric, nonwoven fabric, plastic, thermoplastic, thermoplastic elastomer, elastomer, paper or a combination thereof.

9. The composition of claim 1, 2, 3, 4, 5, 6, 7 or 8, further comprising from 10 to 100 parts by weight of said copolymer.

10. A pressure sensitive adhesive comprising the composition of claim 1, 2, 3, 4, 5, 6, 7, 8 or 9.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 93/09890

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L31/02 C09J131/02 C09D131/02 C08F218/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08L C09J C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 546 640 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 16 June 1993 see page 8; table 1 see claim 11	1,3-8
X	EP,A,0 516 202 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 2 December 1992 see page 6, table see page 6, line 52 - page 7, line 7 see claims 5,6	1,3-8
X	EP,A,0 486 110 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 20 May 1992 see page 7, table see page 8, line 7 - line 26	1,3-8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 1994	10.02.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Siemens, T

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 93/09890

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 432 811 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 19 June 1991 see example 1 -----	1,3-8

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09890

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 2
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 2 not searched because It is referring to itself

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/US 93/09890

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0546640	16-06-93	CA-A-	2085076	14-06-93
EP-A-0516202	02-12-92	JP-A-	5230153	07-09-93
EP-A-0486110	20-05-92	JP-A-	4285612	09-10-92
EP-A-0432811	19-06-91	JP-A-	3170513	24-07-91